# The Effect of Vacuum Carbonization of Waste Maize Stalk on the Thermal Resistance of Polyester/Maize Stalk Particulate Composites

S.B. Hassan[1], J.E. Oghenevweta[*2], G.B. Nyior[3], V.S. Aigbodion[4]

[1,2,3,4] Department of Metallurgical and Materials Engineering, Ahmadu Bello University, Zaria-Nigeria

[1]profsbolajihassan@gmail.com; [*2]joghenevweta@abu.edu.ng; [3]gbnyior2003@yahoo.com.uk; [4]aigbodionv@yahoo.com

## Abstract

The effect of vacuum carbonization of waste maize stalk on the thermal resistance of polyester/maize stalk particulate composites has been investigated. Maize stalk was carbonized at a temperature of 1200°C to convert the biomass into biocarbon; then the carbonized maize stalk was used to reinforce polyester while the uncarbonized ones served as the control. The carbonized maize stalk particulates (CMSp) were added with different volume fractions into a polyester matrix at an interval of 2, 4, 6, 8, and 10% respectively. The thermal resistance of the composites was evaluated using the thermogravimetric (TGA) and differential thermal analysis (DTA). Results from the TGA/DTA examination showed that the resistance to thermal degradation of the carbonized polyester/maize stalk particulate composites is higher than the one that is not carbonized. Also, as the content of the carbonized maize stalk particulate increases, the thermal resistance of the composites increases. This result has indicated that the process of carbonization can enhance the degree of thermal resistance of the polyester/maize stalk particulate composites.

## Keywords

Carbonized Maize Stalk Particulates; Polyester Resin; Thermal Resistance; Thermal Degradation

## Introduction

Heating a material at a steady rate can produce chemical changes, such as oxidation and degradation, and/or physical changes, such as the glass transition in polymers, conversions/inversions in ceramics and phase changes in metals. The various techniques of thermal analysis measure one or more physical properties of a sample as a function of temperature. The three basic methods of thermal analysis are thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Respectively, they measure change in mass (TGA) and energy flow (DTA, DSC), and can apply programmed heating and cooling, but usually operate with a slowly rising temperature. The sample chamber may contain air, oxygen, nitrogen, argon, etc. or be evacuated (Pijpers et al., 2008).

Thermogravimetric analysis or thermal gravimetric analysis (TGA), a type of testing performed on samples that determines changes in weight in relation to change in temperature, is the act of heating a mixture to a high enough temperature so that one of the components decomposes into gas, which dissociates into the air. It is a process in which heat and stoichiometry ratios are utilized to determine the percent by mass ration of a solute. If the compounds in the mixture that remain are known, then the percentage by mass can be determined by taking the weight of what is left in the mixture and dividing it by the initial mass. Knowing the mass of the original mixture and the total mass of impurities liberating upon heating, the stoichiometric ratio can be used to calculate the percent mass of the substance in a sample (Cullity et al., 2001).

Simultaneous TGA-DTA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events with no associated weight loss (e.g. melting and crystallization) and those that involve a weight loss (e.g. degradation) (Czichos et al., 2006).

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to

estimate the corrosion kinetics in high temperature oxidation (Pijpers et al., 2008).

The morphology and the mechanical properties of carbonized waste maize stalk reinforce polyester composites with the aim of producing an eco-friendly composite material showing enhanced properties for engineering applications has been investigated. The results showed that there is enhanced tensile strength, tensile modulus and compressive strength values as the carbonized maize stalk ash content increases (Hassan et al., 2012)

The aim of this research is to investigate the effect of vacuum carbonization of maize stalk ash particles reinforced polyester composites in order to develop a thermal resistance engineering material for novel configurations in automotive industries such as radiator grids and heat resistance car body panels.

## Materials/Equipment

The maize stalk used was obtained from a harvested agricultural farm in Samaru, Zaria-Kaduna State, Nigeria. The base polyester resin, accelerator (Cobalt Octoate) and catalyst (Methyl ethyl Ketone Peroxide (MEKP)) was obtained from Steve Moore Chemicals, Zaria-Kaduna State, Nigeria.

The equipment used in this research include electric milling machine, electric resistance furnace, graphite crucible, digital weighing balance, beakers, glass rod stirrers, hand gloves, and simultaneous DTA/TGA analyzer (Model Orton ST-736)

## Methods

### Characterizations of the Carbonized Maize Stalk Particles

#### 1) Maize Stalk Preparation

The maize stalk tegument was chopped into smaller sizes and then dried in the sun. The dried stalks were ground to a fine powder using electrical milling machine. The fine powder was carbonized at a temperature of $1200^0$C in an electric resistance furnace in order to form the carbonized maize stalk particulates.

#### 2) Sieved Size Analysis of the CMSp

The maize stalk particulates was then sieved unto a set of sieves arranged in descending order of fineness and particle size analysis was carried out in accordance with BS 1377:1990. A particle size of 53 μm was selected and used.

#### 3) Microstructural and Phase Examination of the CMSp

The microstructure of the carbonized maize stalk particles (CMSp) was analyzed using the scanning electron microscope (SEM) equipped with an Orton INCA™ energy dispersive spectrometer (EDS).

The various distributions of phases in the CMSp were analyzed by using X-ray diffractometer (RXD). The X-ray diffractograms was taken using Cu $K\alpha$ radiation at scan speed of $3^o$Co/ mins. The CMSp was rotated at precisely one-half of the angular speed of the receiving slit so that a constant angle between the incident and reflected beams is maintained. The receiving slit is mounted on the counter tube arm, and behind it is usually fixed a scatter slit to ensure that the counter receives radiation only from the portion of the specimen illuminated by the primary beam. The intensity diffracted at the various angles was recorded automatically on a chart and the appropriate (θ) and (d) values were obtained

### Synthesis of the Composites

In producing the reinforced polyester composites, the unsaturated polyester was measured into a 400 ml beaker and heated to $150^0$C and the carbonized maize stalk was added and then stirred vigorously until even dispersion was achieved. Addition of 1% weight of catalyst was made and stirred vigorously for another 3 min. Moreover, 2% weight of accelerator was added to the mixtures and stirred vigorously for another 3 min before casting the sample into a mould. Initially, the mould was cleaned with acetone and coated with polyvinyl alcohol (PVA) and allowed to dry before the sample was cast. This procedure was repeated for all samples produced with changes in the percentage of the carbonized maize stalk particles.

### Thermal Examination of the Polyester/CMS Particulate Composites

The simultaneous thermogravimetric analysis (TGA)/ differential thermal analysis (DTA) was carried out in the Department of Chemical and Metallurgical Engineering, University of Johannesburg, South Africa. The samples were evenly and loosely distributed in an open sample pan of 6.4 mm diameter and 3.2 mm depth with an initial sample amount of 8-10 mg. Due to different bulk density, the depth of the sample layer filled in the pan was about 1-2 mm. The temperature

change was controlled from room temperature (25±3°C) to 700°C at a heating rate of 10°C/min. The sampling segment was set at 0.5 second per point.

High pure argon was continuously passed into the furnace at a flow rate of 60 ml/min at room temperature and atmospheric pressure. Before starting each run, the Argon was used to purge the furnace for 30 min to establish an inert environment in order to prevent any unwanted oxidative decomposition. The TG and DTA curves that were obtained from TGA runs were carefully smoothed at a smoothing region width of 0.2°C by using least squares smoothing method, and analyzed by using Universal Analysis 2000 software from TA Instruments.

## Results and Discussion

The results of test conducted on the control and the developed composites are presented as follows: Plate 1 shows the particle size analysis of carbonized maize stalk particulate, Plate 2 shows the SEM microstructure of the CMSp while Plate 3 shows the EDS of the CMSp. Plate 4 shows the XRD of the CMSp while Pale 5 shows the TGA/DTA analysis of the polyester resin. Plates 6-10 show the TGA/DTA of the carbonized maize stalk particulate/polyester composites at 2-10wt% maize stalk additions.

### Particle Size Analysis of the CMSp

Plate 1 shows the particle size distribution of the maize stalk ash sample. The grain fineness number (GFN) of sample was computed to be equal to 92.12. Based on this value, the sample is considered to be fine since GFN of 100 is ranked the most fine. Besides, four mesh sieve sizes contained the bulk of the retained sample on four consecutive sieves corresponding to 185 μm, 125 μm, 100 μm and 53 μm size fractions therefore, the sample has met the America Foundrymen's Society (AFS) specification. Particles that were retained in 53 μm mesh size were selected for this research because it contained high volume of sieved MSA particles (see Plate 1).

### SEM, EDS and XRD Analysis of the CMSp

The microstructure of the CMSp as obtained from SEM analysis is shown in Plate 2, which clearly reveals the particle sizes and shapes. The orientation of these particles could be grouped into fibrous, prismatic and spherical. In terms of the classification of these particles, the fibrous ones are usually consist mainly of carbon (C), the prismatic ones consist of potassium (K), magnesium (Mg) and silicon (Si) while the spherical consist of elemental oxygen [O]. The fibrous grains shape has defined edges, and the surfaces are nearly flat. They produce the highest strength at the interface between the matrix and the reinforcement; the prismatic ones have comparatively lower strength than the fibrous but higher than the spherical shapes, while the spherical ones have the least contact with one another in the mixture and also between the matrix and the reinforcement thereby lacking strength and being not pack up to the optimum extent (Felix, 2003).

From the EDS spectrum (see Plate 3), it can be seen clearly that the elemental compositions of the CMSp consist of carbon (At% 89.32), oxygen (At% 5.10), magnesium (At% 0.35), potassium (At% 4.41) and silicon (At% 0.64) but the atomic weight of carbon is the highest.

The X-ray diffraction pattern obtained for CMSp (see Plate 4) displays numerous diffraction peaks which reflect the diffraction intensities. It can be observed that the phases at these peaks are silicon oxide ($SiO_2$) and carbon, (C). The presence of this amorphous carbon in the carbonized maize particle which does not easily burn off in oxidative medium could possibly lead to delaying the thermal degradation of polymer composites.

### The Effect of Carbonized Maize Stalk Particulates on the Thermal Resistance of the Developed Composites

Thermogravimetric analysis (TGA) of the polyester resin and the carbonized polyester/CMSp composites were studied as a function of percentage weight loss as the temperature increased (see Plate 5 and Plates 6-10 respectively).

TGA analysis has been performed in an oxidative atmosphere (air or oxygen and inert gas mixtures) with a linear temperature ramp (see Plates 5-10). The maximum temperature is selected so that the specimen weight is stable at the end of the experiment, implying that all chemical reactions are completed (i.e., all of the polymer molecules is burnt off leaving behind oxides). This approach provides two important numerical pieces of information: residual mass and oxidation temperature. Oxidation temperature, $T_o$, can be defined in many ways, including the temperature of the maximum in the weight loss rate (dm/dTmax) and the weight loss onset temperature ($T_{onset}$). The former refers to the temperature of the maximum rate of oxidation;
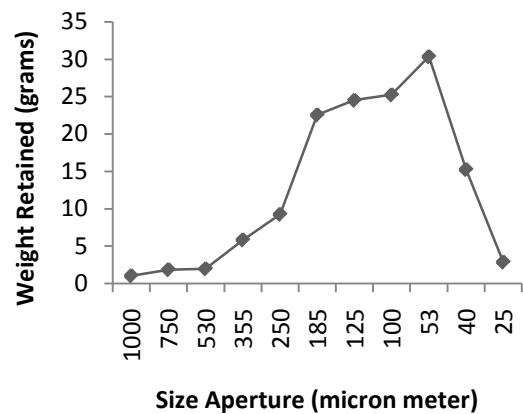
PLATE 1 PARTICLE SIZE ANALYSIS OF THE MAIZE STALK PARTICULATES
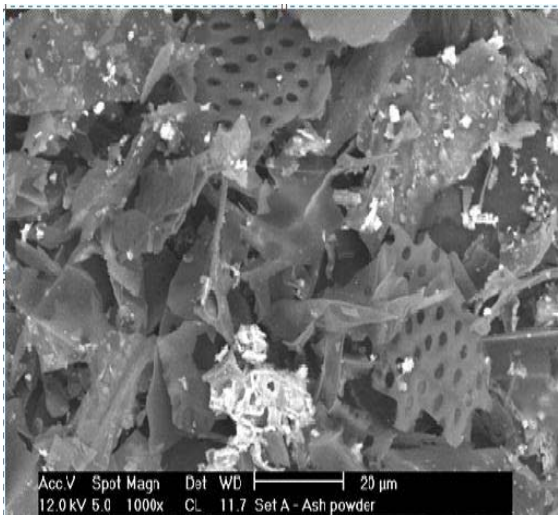


PLATE 2 SEM MICROSTRUCTURE OF THE MAIZE STALK PARTICULATES
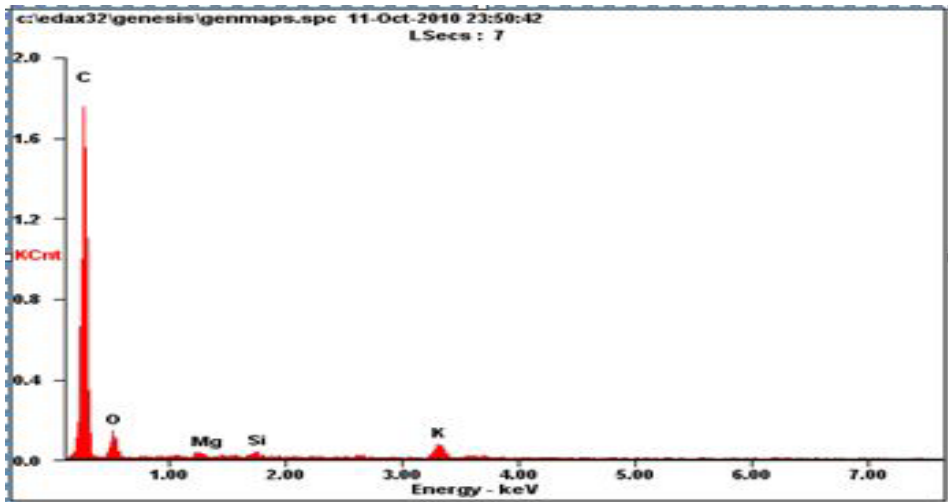


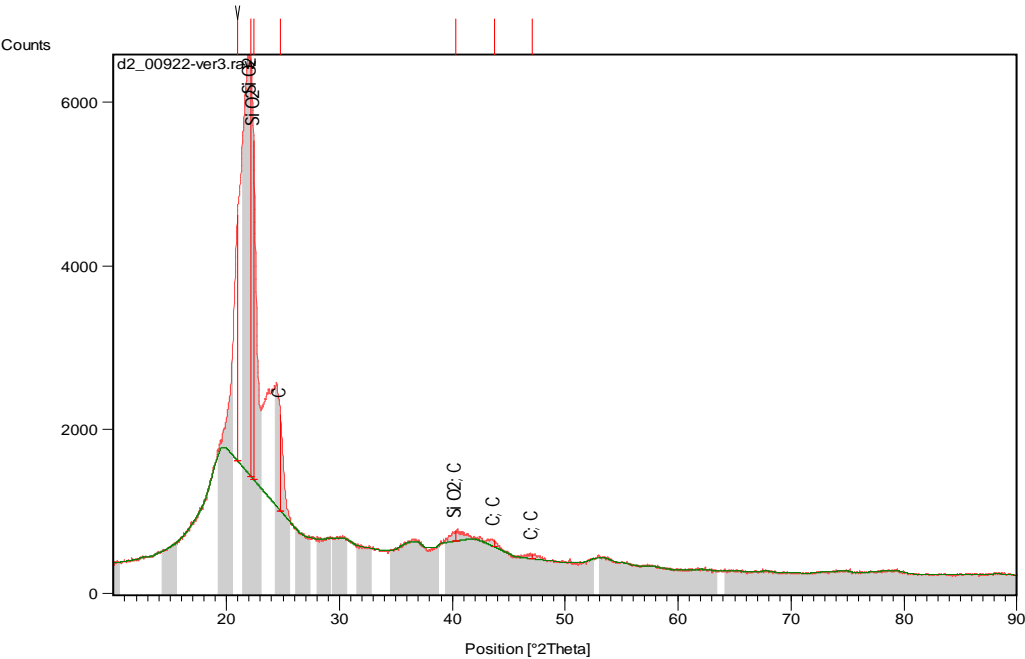PLATE 3 EDS ANALYSIS OF THE MAIZE STALK PARTICULATES



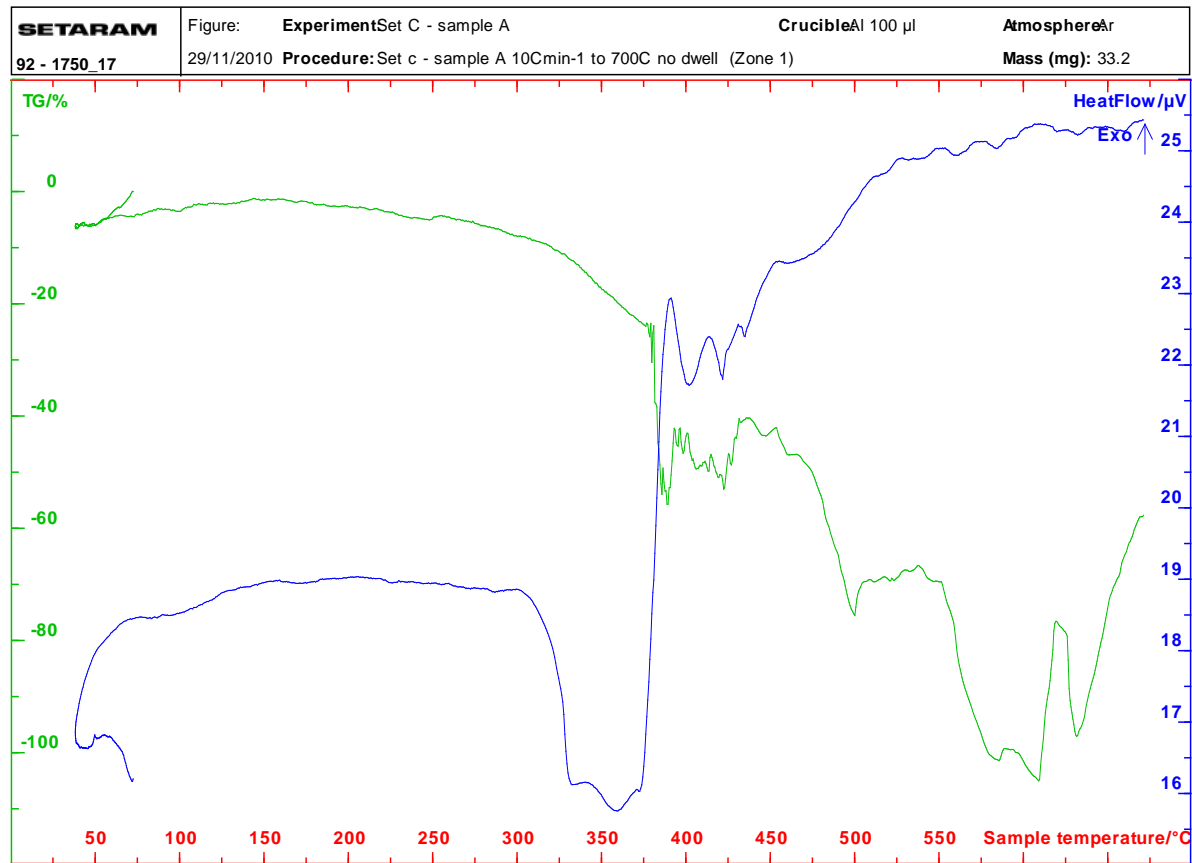PLATE 4 XRD ANALYSIS OF THE MAIZE STALK PARTICULATES

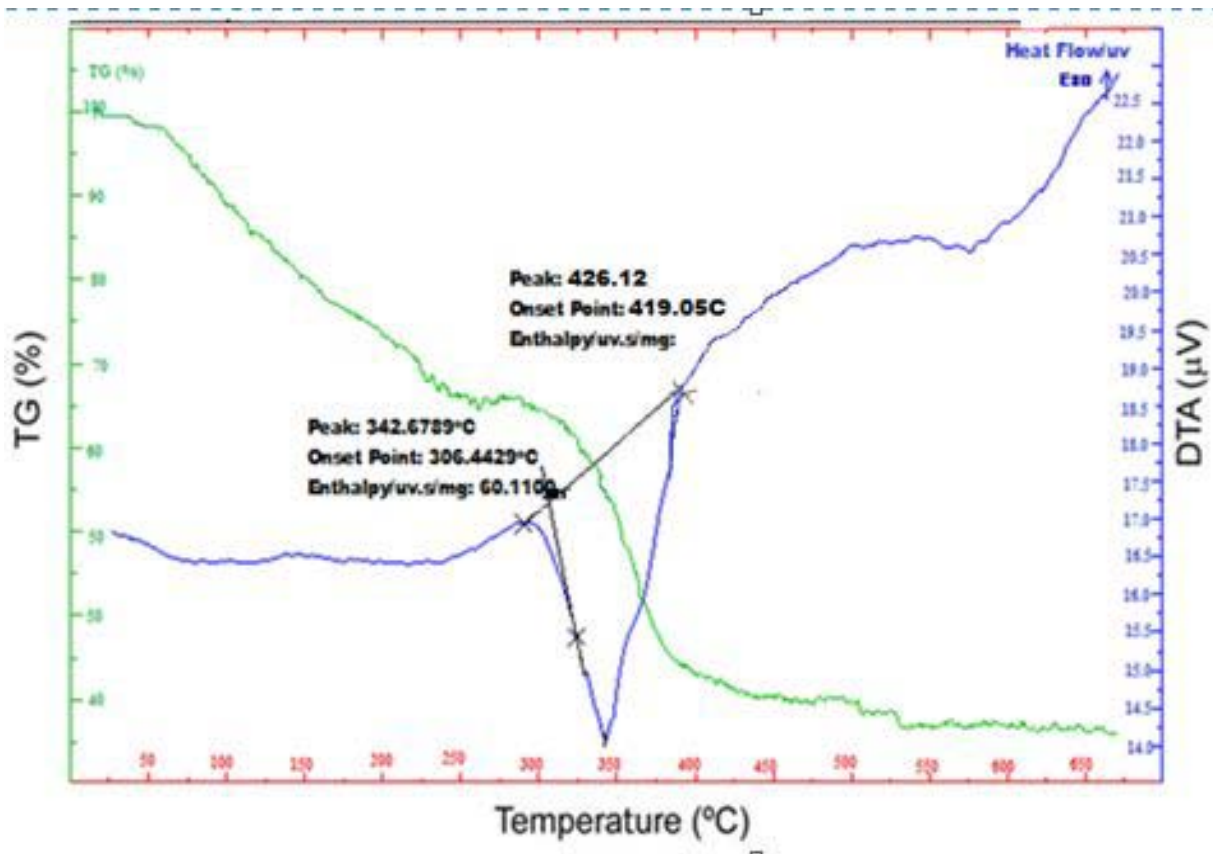PLATE 5 DTA/TGA ANALYSES OF THE POLYESTER RESIN



PLATE 6 DTA/TGA ANALYSES OF THE POLYESTER/2%CMSP COMPOSITE
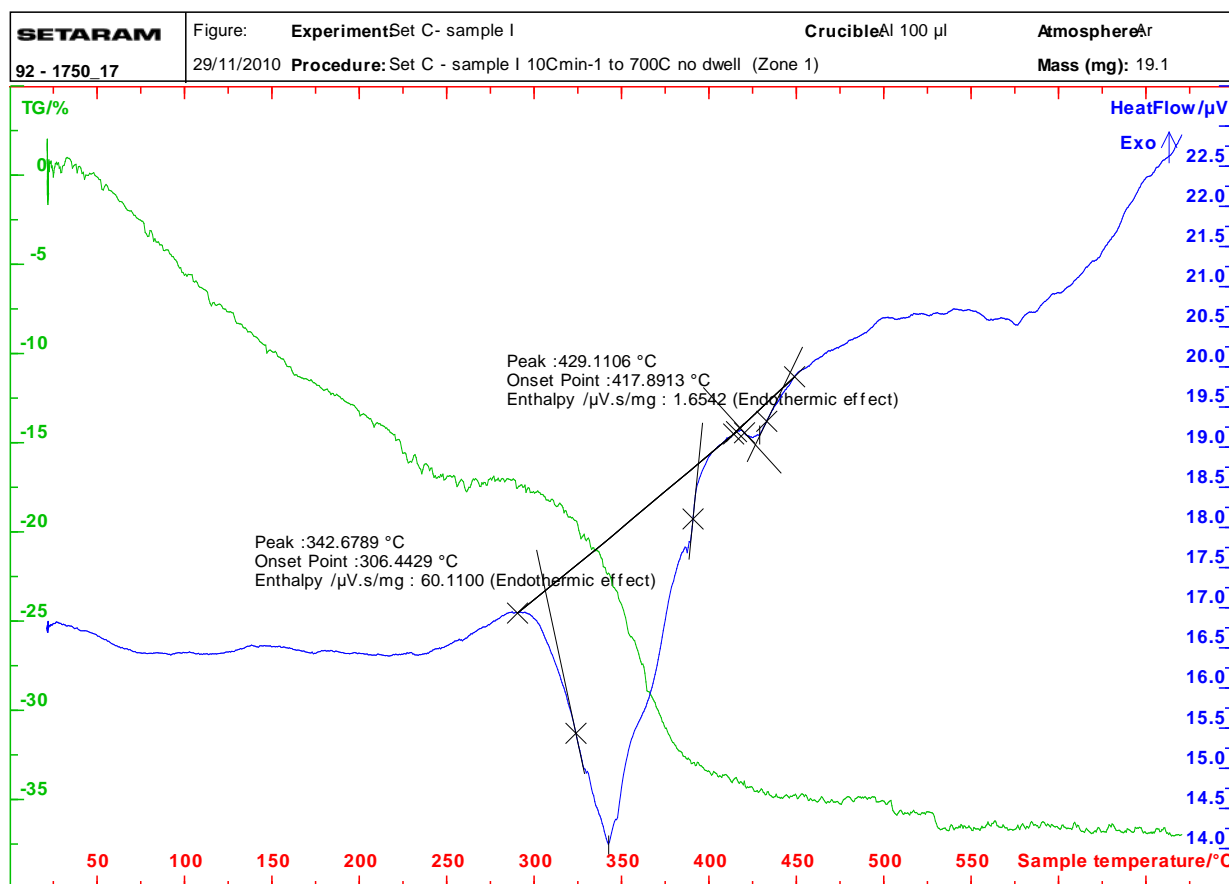
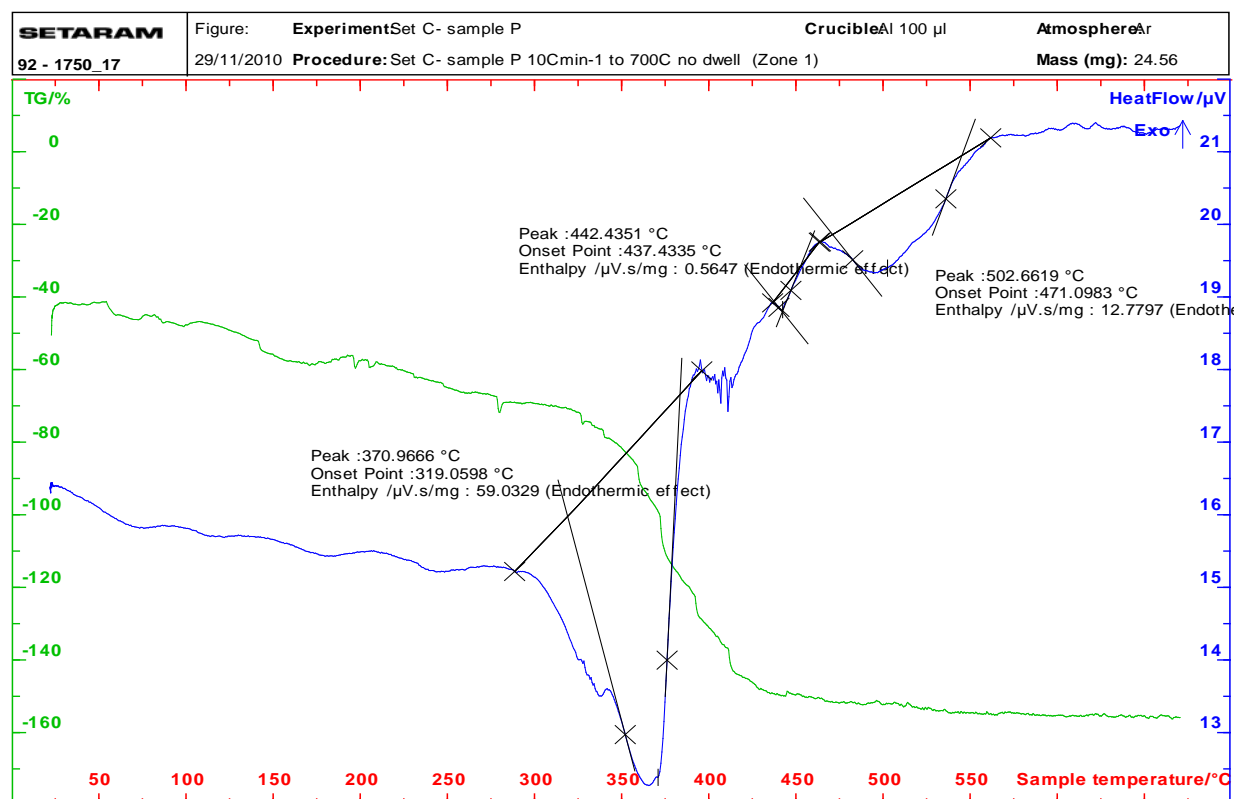PLATE 7 DTA/TGA ANALYSES OF THE POLYESTER/4%CMSP COMPOSITE



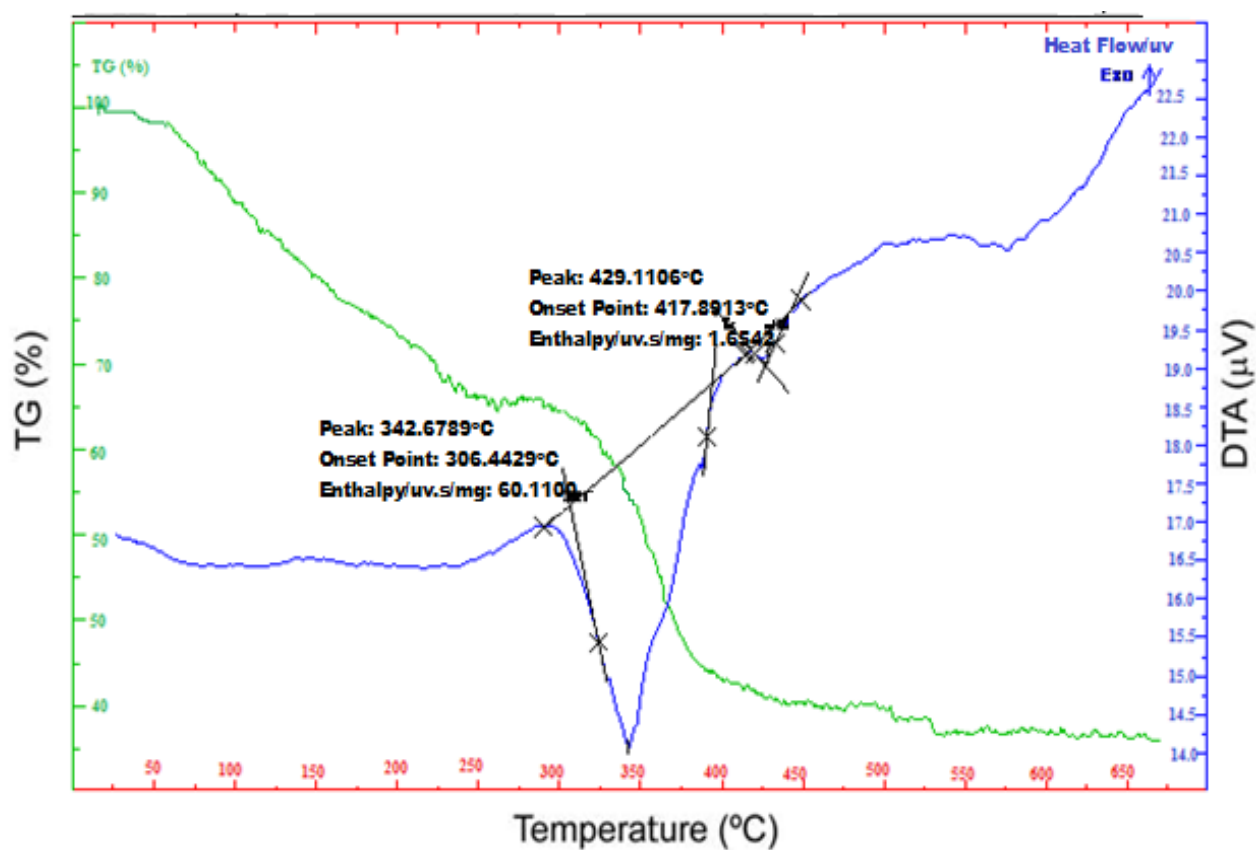PLATE 8 DTA/TGA ANALYSES OF THE POLYESTER/6%CMSP COMPOSITE

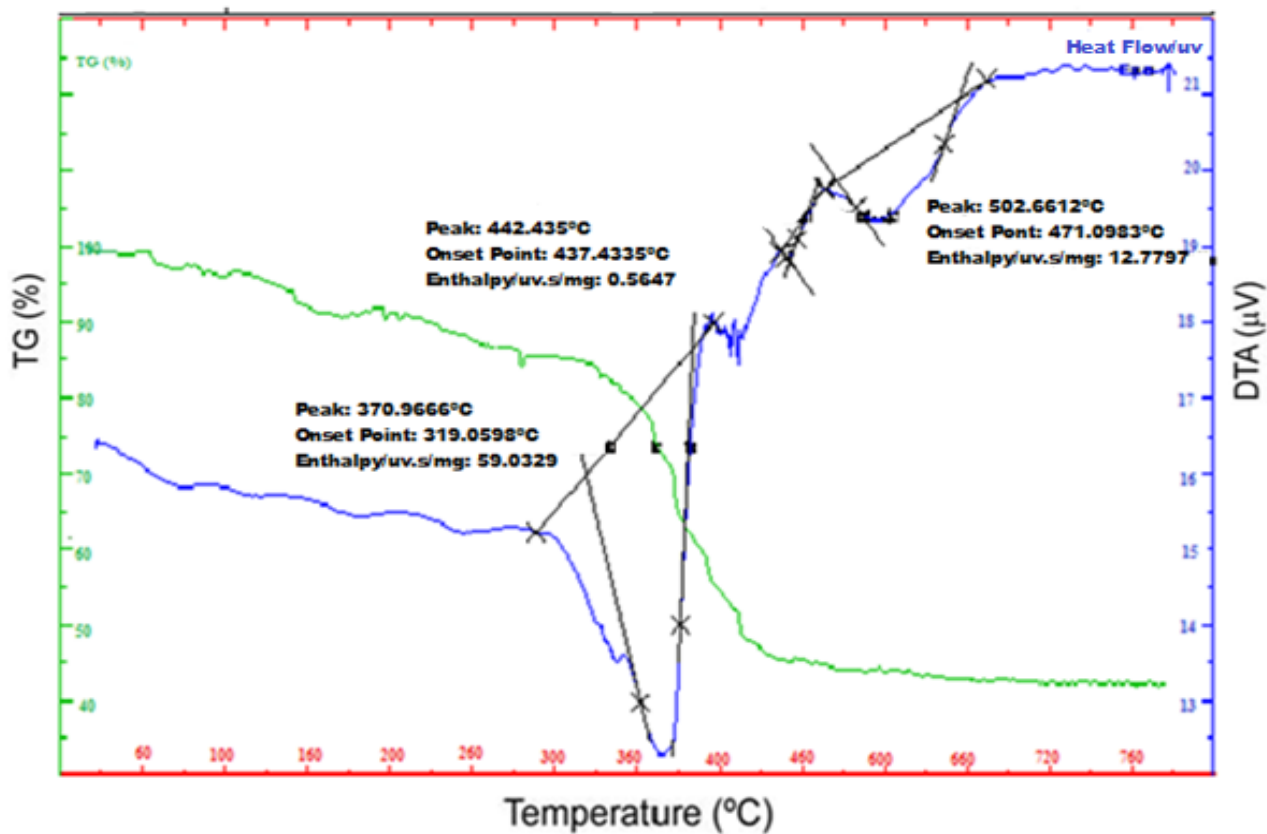PLATE 9 DTA/TGA ANALYSES OF THE POLYESTER/8%CMSP COMPOSITE



PLATE 10 DTA/TGA ANALYSES OF THE POLYESTER/10%CMSP COMPOSITE

while the latter refers to the temperature when oxidation just begins. The use of the former definition, $To$=dm/dTmax, is preferred for two reasons. First, due to the gradual initiation of transition, it may be difficult to determine $T_{onset}$ precisely. Gradual onset is believed to be due to composite reinforced with amorphous carbon and other types of carbonaceous impurities that oxidize at temperatures higher than that of the polyester resin. In these cases, $T_{onset}$ describes the properties of the impurities rather than the matrix. Second, weight loss due to carbon oxidation is often superimposed on the weight increase due to oxidation at low temperatures. In some cases, this leads to an upward swing of the TGA curve prior to the bulk of the weight loss.

Oxidation temperature, $To$, is basically a measure of the thermal stability of polyester/CMSp composites in air and depends on a number of parameters. For example, smaller diameter polyester/CMSp composites are believed to oxidize at lower temperature due to a higher curvature strain. Active functional groups present in the composite may catalyze carbon oxidation, so the amount of impurities in the sample can have a considerable influence on the thermal stability. It is impossible to distinguish these contributions, nevertheless, thermal stability is a good measure of the overall quality of a given polyester/CMSp composite sample.

Considering the polyester resin, the process of depolymerisation commences between the temperature ranges of 100ºC-160ºC followed by cleavages of C-H, C-C and C-O bonds (see Plate 1) while the initial and final decomposition temperature (IDT) t (FDT) of this composite occur at 300ºC and 675ºC respectively (see Plate 5).

On the other hand, the polyester/CMSp composites generally have an initial decomposition temperature ranges of 320-328ºC and final decomposition temperature of 800-818ºC (see Plates 6-10). The increase in the value of the initial and final decomposition temperature is attributed to carbon, silica and graphite on the interface of the polyester/CMSp composite which does not easily burn off in oxidative medium thereby delaying the thermal degradation of the polyester/CMSp composite.

However, analysis of polyester/CMSp composite using DTA produces various peaks that are likely due to the fact that the composite contains a fraction of carbon and/or with functional groups (i.e., the material is oxidized at higher temperature). The positions of each of these peaks are strongly affected by the amount and morphology of these carbon-based impurities, as well as their distribution within the sample. A lean oxygen environment can be used to better separate these peaks. In addition, these peaks have also been attributed to various components in the composite material (amorphous carbon, graphitic particles), and it may be possible to quantify these components by de-convolution of peaks.

Also, it was observed that these peaks contain exothermic and endothermic reactions at different temperatures. The magnitude and location of these peaks show that there is a change in the thermal behaviour between the unreinforced polyester and the polyester/CMSp composite since these peaks are function of the change in enthalpy ΔH) as well as the mass of the samples. The change in enthalpy indicates the energy differences between the activated complex and the transition temperatures.

Besides, it was observed that for the polyester/ uncarbonized maize stalk particulates has zig-zag change in enthalpy compared to the polyester/CMSp composites which have relatively defined change in the enthalpy changes. This uniform change in the enthalpy may be due to chemical reactions occurring at a faster rate and shorter time for the later than that for the former which takes longer time to form the activated complex. This study has showsn that vacuum carbonization can lead to composites that are thermally stable as compared to those that are carbonized. This observation is in agreement with earlier research by Tavman (1996); Tyan (1999); Chung (2000) and Vijay et al. (2010).

## Conclusions

From the thermogravimetric and differential thermal analyses of the polyester/carbonized maize stalk particulate composites, it can be shown that vacuum carbonization of maize stalk ash can be used as source to enhance the thermal stability polymer reinforce maize stalk particulate composites. This research has added novel information on the method to improve the thermal stability of polymer composites. Therefore, it can be concluded from the results obtained that the developed composites have shown improved thermal stability as compared with the uncarbonized maize stalk/polyester composites.

### REFERENCES

Ahmad, F.M.Y., Mohammed, I.Z.A., Omar, A.K., Mustafah, J.

and Mansor, M.S. "Thermal Properties of Polypropylene/ Rice Husk Ash Composites". Polymer Interphase Journal (1995) **38**(1): 33-34.

Chung, D. D. "Thermal Analysis of Carbon Fiber Polymer-matrix Composites by Electrical Resistance Measurement". Journal of Thermochimica Acta (2000) 364(1): 121-132.

Cullity B.D.; Stock S.R. "Elements of X-Ray Diffraction" 2nd Edition. Published by Prentice Hall: New Jersey, 2001, pp. 567-892.

Czichos E.Y., Saito B., Smith E. (2006): Materials Measurement Methods; Springer: 411–413.

Felix, U. "Maize-cob Ash as Filler in Concrete". Journal of Materials in Civil Engineering, 2003 15(2): 205-208.

Hassan S.B., Oghenevweta J.E. and Aigbodion, V.S. "Morphological and Mechanical Properties of Carbonized Waste Maize Stalk as Reinforcement for Eco-composites" Journal of Composites Part B. Engineering. Elsevier,

(2012) 43B (5): 2230-2236.

Pijpers, M. F. J., and Mathot, V. B. F. "Optimisation of Instrument Response and Resolution of Standard – and High Speed Power Compensation DSC." Journal of Thermal Analysis and Calorimetry, (2008) 93(3): 319–327.

Tayman, I. H.. "Thermal and Mechanical Properties of Aluminium Powder-filled High Density Polyethylene Composites. *Journal of Applied Polymer Science*, (1996) 62(1): 2161-2167.

Tyan, H.L., Liu, Y.C., and Wei, K.H. "Thermally and Mechanically Enhanced Clay/Polyimide Nanocomposite via Reactive Organoclay". Chemical Materials Journal *(1999)* 11(1): 1942–1947.

Vijay, K. T., and Amar, S.S. "Physico-chemical and Mechanical Characterization of Natural Fibre Reinforced Polymer Composites." Iranian Polymer Journal, (2010). 19(1): 3-16.